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Estimation of Octanol/Water Partition Coefficients for Organic Pollutants Using Reverse-Phase HPLC

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ESTIMATION OF OCTANOL/WATER PARTITION COEFFICIENTS FOR ORGANIC POLLUTANTS USING REVERSE-PHASE HPLC

Bruce McDuffie*
Environmental Research Laboratory
U.S. Environmental Protection Agency
College Station Road
Athens, Georgia 30613

ABSTRACT — Octanol/water partition coefficients (K_{ow}'s) of organic solutes are estimated with reasonable accuracy (standard deviation ± 0.25 log K_{ow} units) by elution from a C-18 column with 75:25 (v/v) MeOH-H_2O, based on results with 37 test compounds. Changes in solute activity coefficients from water to 75% MeOH account for the slope of the log K_{ow}-log k' plot, where k' is the HPLC capacity factor. The method is used to estimate K_{ow}'s for 25 additional organic compounds, and some disparities between the results and those calculated using group additivity-constitutive factors are noted.

INTRODUCTION

The 1-octanol/water partition coefficient, K_{ow}, is a useful parameter for characterizing the lipophilicity or hydrophobicity of organic compounds (1-3). Further, studies of organic pollutants show strong correlations between K_{ow} and K_{oc}, the constant for partitioning of a pollutant from water into the organic carbon fraction of a soil or sediment (4-6) and between K_{ow} and BCF, the bioconcentration factor for uptake of a pollutant by an aquatic organism (7-9). These correlations, which increase one's ability to model the fate of organic pollutants in aquatic ecosystems, give added importance to methods for the determination or reliable estimation of K_{ow} values.

Direct determinations of K_{ow}, using the conventional shake-flask method, are subject to numerous experimental difficulties (10). Reverse-phase high performance liquid chromatography (HPLC), with C-18 columns, has been applied by several workers to the rapid indirect estimation of partition coefficients from retention data. Relatively polar mobile phases were used for compounds with K_{ow}'s of 10^1 to 10^3 (11, 12), and up to 80% MeOH in H_2O was used for drugs with K_{ow}'s as high as 10^5 (13). Finally, the direct chromatographic determination of K_{ow}'s, using various octanol-coated columns and octanol-saturated water as mobile phase, has been demonstrated (14-16), but the columns require periodic re-coating, and retention times for solutes with $K_{ow} > 10^2$ are inconveniently long unless very short columns (<10 cm) are used.

Veith et al. (17) applied the indirect chromatographic method to organic pollutants using a C_{18}-column and an 85:15 (v/v) MeOH-H_2O solvent mixture. They estimated K_{ow}'s from chromatographic retention times, t_R, plotting log K_{ow} versus log t_R and calibrating the method with six compounds having K_{ow} values from 10^2 to 10^6. From measurements on a series of compounds, the standard deviation in log K_{ow} values (compared to literature values) was around 0.6 units. This approach was extended to compounds with $K_{ow} > 10^6$ by Entz (18), using a 90:10 MeOH-H_2O mixture.

In chromatographic elution theory, partitioning of a solute from the mobile phase into (or onto) the stationary phase increases the time that the substance spends in the column, compared to solvent molecules. If injected solvent reaches the detector in a time, t_o, then the extra time that the solute peak spends in the column is given by the equation

$$t_R - t_o = t_c \qquad (1)$$

*Present Address: Laboratory for Trace Methods and Environmental Analysis, Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13901.

where t_c is the corrected retention time. The ratio t_c/t_o (called the capacity factor, k') gives the molecular or weight distribution of the solute between the two phases. It is independent of flow rate, under ideal chromatographic conditions, but is a function of the nature of the stationary phase and of the eluting solvent, both of which affect the chromatographic partitioning tendency.

Anticipating results to be presented below, we note that solutes with K_{ow}'s differing by many orders of magnitude have k' values in MeOH-H_2O that cover a much smaller range. Assuming a power relationship, we write

$$K_{ow} \propto k'^{b} \tag{2}$$

or in logarithmic form

$$\log K_{ow} = b \log k' + c \tag{3}$$

where c is the logarithm of the proportionality constant for eq. 2.

This hypothesis of a power relationship between K_{ow} and k', leading to a linear correlation between log K_{ow} and log k', will be explored for various organic solutes using several eluting solvents. It is a well known feature of liquid chromatographic separations that resolution can often be improved by changing the solvent, a consequence of the fact that the relative k' values for solutes may change from one solvent medium to another. Thus, an objective of the present research was to find a medium in which the k' values for organic pollutants would be in the same relative order as their K_{ow} values.

EXPERIMENTAL

Chromatographic grade methanol (Burdick and Jackson, distilled-in-glass) and doubly-distilled water were used to prepare eluting solvents, which were degassed by sonication before use. Isocratic elution with 100% MeOH, 85:15 (v/v) MeOH-H_2O, or 75:25 (v/v) MeOH-H_2O was used. The organic compounds to be tested, generally 99+% pure, were obtained from Aldrich Chemical Company, Analabs, J. T. Baker, Chem Service, Chemicals Procurement Laboratories (College Point, NY 11356), and the U.S. EPA Health Effects Research Laboratory, (Research Triangle Park, NC 27711). Compounds were dissolved in MeOH, MeOH-H_2O mixtures, or occasionally in a less polar solvent such as hexane (for the least water-soluble compounds), to prepare solutions sufficiently concentrated (1 to 50 ppm) for chromatographic detection with a 20 µL injection.

The liquid chromatograph was a Tracor instrument equipped with a Model 950 Chromatographic Pump, a Model 970A Variable Wavelength Detector, and (in series) a Model 965 Photo-Conductivity (PC) Detector with Hg lamp. A Zorbax-ODS C_{18}-microparticulate column, 0.46 x 25 cm (DuPont Company) with CO:Pell ODS guard column (Whatman, Inc.) was used with flow rates of 1.0 and 2.0 ml/min. at ambient temperature (25±3°C). Values of t_o for these flow rates were 2.5 and 1.25 min., respectively, determined from the t_R of formamide (11). Various wavelengths were used, as appropriate, with full-scale recorder ranges from 0.02 to 1.28 absorbance units (AU). If photolysis occurred, the ratio of peak detector responses for the solutes ranged from 10^4 to 1 AU/mV PC response. Ultraviolet responses were nearly independent of flow rate, but PC responses (if they occurred) generally increased as flow decreased, because of increased time spent by the solute in the photolysis reaction cell.

RESULTS AND DISCUSSION

In preliminary experiments using the method of Veith et al. (17), we observed that an improved linear correlation was obtained when log K_{ow} was plotted against log t_c rather than against log t_R. This is consistent with chromatographic theory as discussed above. As pointed out by McCall (11), the difference between a log t_c and a log t_R plot is especially great for compounds with short retention times; for example, at a flow rate of 1.0 mL/min. in 85:15 (v/v) MeOH-H_2O, benzene had a t_R of 4.2 min. and a t_c of 1.7 min., giving log values of 0.62 and 0.23, respectively. Figure 1 shows how a linear (idealized) log K_{ow}-log t_c plot becomes a curved log K_{ow}-log t_R plot (assuming t_o = 2.5 min.).

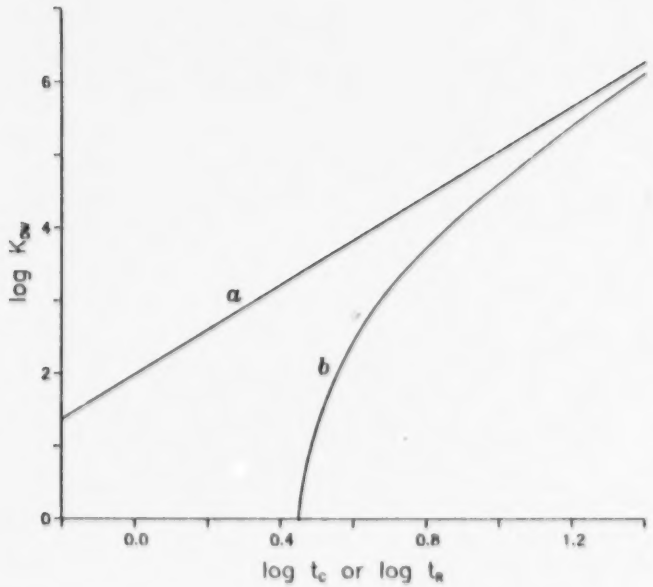

Figure 1. Effect of Using Uncorrected Retention Time in Log K_{ow} Plots
a. Log K_{ow} versus log t_c. b. Log K_{ow} versus log t_R.

It was evident also from preliminary experiments that k' could be used instead of t_c to compare data taken at different flow rates, as is generally necessary when using various solvent mixtures and compounds covering a wide range of K_{ow} values. Thus, plots of log K_{ow} versus log k' were used to normalize data taken at different flow rates.

To examine the solvent effect, 10 pollutants were chromatographed in 100% MeOH, in 85:15 MeOH-H_2O, and in 75:25 MeOH-H_2O. Figure 2 shows how the log k' values changed for this group of solutes, the k' values being normalized by the k' for phenanthrene. The pattern appears regular for the polynuclear aromatic hydrocarbons (presumably because of the phenanthrene normalization), whereas in contrast the relative log k' values and even the elution orders change drastically for methoxychlor, p,p'-DDT, and 2,5,3',4'-tetrachlorobipnenyl. It is clear that the solvent composition has a significant effect on relative k' values. Figure 2 also shows that the data for 75:25 (v/v) MeOH-H_2O correlate reasonably well with the log K_{ow} values for these solutes. [The log K_{ow} value for 2,5,3',4'-tetrachlorobiphenyl was estimated from a K_{OC} value (19), using the method of Karickhoff *et al.* (4), thus is not as reliable as one determined by the direct method.]

Changes in relative k's with changing solvent composition reflect changes in relative activity coefficients for the solutes in the different media and, in principle, may be calculated or predicted from solubility data (see below).

Correlation Studies

Additional solutes were run in the 75:25 medium to establish the strength of the log K_{ow}-log k' correlation. Data for 15 organic compounds, including 7 aromatic hydrocarbons, 5 halogenated aromatic derivatives, and 3 triazines are presented in Table I, Part A, arranged in the order of increasing log $k'_{75:25}$ values. Linear regression for the 75:25 data gave the following equation.

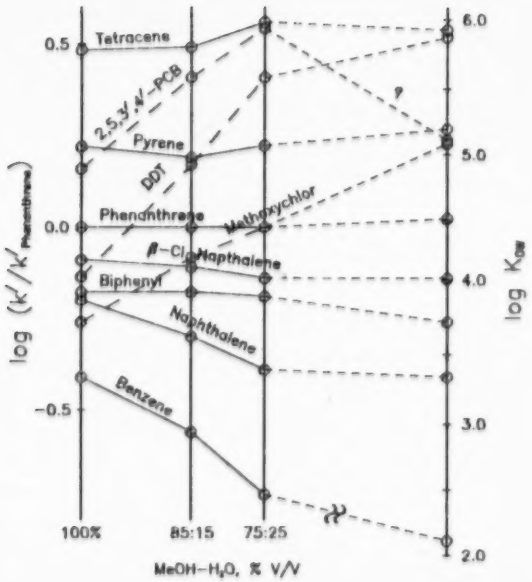

Figure 2. Effect of % MeOH on Elution Order and K_{OW} Correlation.
$k'/k'_{phenanthrene}$ = capacity factor relative to phenanthrene.

$$\log K_{OW} = 2.61\ (\pm 0.13)\ \log k'_{75:25} + 2.55\ (\pm 0.11) \qquad (R^2 = 0.968) \qquad (4)$$

where R^2 is the correlation coefficient. The errors in predicting log K_{OW} values using eq. 4 are shown in Table I, Part A, Column 5. For data in the 85:15 medium, linear regression yielded the equation

$$\log K_{OW} = 3.02(\pm 0.24)\ \log k'_{85:15} + 3.33\ (\pm 0.12) \qquad (R^2 = 0.927) \qquad (5)$$

It is evident from the R^2 values that the correlation was stronger in the 75:25 than in the 85:15 medium. Further, the standard deviations in Δlog K_{OW} values (not shown in Table I, Part A, for eq. 5) were 0.24 and 0.37, respectively, for the two media.

Table I, Part B presents data on 22 additional solutes with known log K_{OW}'s that were chromatographed in the 75:25 MeOH-H_2O medium. Retention times as well as log k' data are given in the alphabetical listing, which includes 9 halogenated aromatics, 4 halogenated aliphatics, and 8 aromatic derivatives containing a variety of functional groups. The average Δlog K_{OW} (using eq. 4) was 0.27, somewhat larger than for the 15 compounds of Table I, Part A, but the deviations were mostly positive. A separate linear regression on these 22 compounds gave a line with R_2 = 0.979 and a slope of 2.64, approximately the same as in eq. 4, but with an intercept significantly lower (2.31 versus 2.55), explaining the uniformly positive deviations when eq. 4 was used.

Linear regression for all 37 compounds of Table I, as shown in Figure 3, gave the following result,

$$\log K_{OW} = 2.70\ (\pm 0.07)\ \log k'_{75:25} + 2.37\ (\pm 0.05) \qquad (R^2 = 0.975) \qquad (6)$$

Table I. Chromatographic Data in 85:15 and 75:25 (v/v) MeOH-H_2O, Correlated with K_{ow} Data

No.	Compound	85:15 Medium	75:25 Medium		Lit.	$\Delta \log K_{ow}$[b]	
		log k'	t_R(min)[a]	log k'	log K_{ow}	using Eq. 4	using Eq. 6
		(1)	(2)	(3)	(4)	(5)	(6)
Part A							
1.	Simazine	-0.44	4.10(1)	-0.19	2.16[c]	-0.10	-0.30
2.	Atrazine	-0.34	4.70(1)	-0.06	2.71[c]	-0.31	-0.50
3.	Benzene	-0.17	5.10(1)	0.02	2.11[d]	0.49	0.32
4.	Trietazine	0.02	7.90(1)	0.33	3.35[c]	0.06	-0.08
5.	Naphthalene	0.12	4.25(2)	0.38	3.36[d]	0.18	0.04
6.	Biphenyl	0.26	5.85(2)	0.57	4.09[e]	-0.05	-0.18
7.	a-Cl-Naphthalene	0.31	6.50(2)	0.62	4.07[f]	0.10	-0.02
8.	Phenanthrene	0.45	17.30(1)	0.77	4.57[d]	-0.01	-0.12
9.	Methoxychlor	0.37	9.00(2)	0.79	5.08[d]	-0.47	-0.57
10.	Anthracene	0.52	9.50(2)	0.82	4.54[d]	0.15	0.05
11.	Trifluralin	0.46	23.9 (1)	0.93	5.28[c]	-0.30	-0.39
12.	Pyrene	0.62	13.50(2)	0.99	5.18[d]	-0.05	-0.13
13.	p,p'-DDT	0.67	20.0 (2)	1.18	5.57[g]	0.06	-0.01
14.	Tetracene	0.82	29.0 (2)	1.35	5.90[d]	0.17	0.12
15.	2,4,6,2',4',6'-PCB	1.07	39.4 (2)	1.48	6.34[d]	0.07	0.03
					Av (n=15)	0.17	
Part B							
16.	Acetophenone		1.88(2)	-0.30	1.58[e]	0.19	-0.02
17.	Benzophenone		3.05(2)	0.18	3.18[e]	-0.16	-0.32
18.	Bromobenzene		3.70(2)	0.29	2.99[e]	0.32	0.17
19.	Carbon tetrachloride		6.55(1)	0.21	2.73[h]	0.37	0.21
20.	Chlorobenzene		6.35(1)	0.19	2.84[e]	0.21	0.05
21.	Chloroform		4.05(1)	-0.21	1.97[e]	0.03	-0.16
22.	1,2-Dichlorobenzene		9.00(1)	0.41	3.38[e]	0.24	0.10
23.	1,3-Dichlorobenzene		9.70(1)	0.46	3.38[e]	0.37	0.24
24.	1,4-Dichlorobenzene		4.50(2)	0.41	3.39[e]	0.23	0.09
25.	Dimethylphthalate		1.90(2)	-0.28	1.61[i]	0.21	0.01
26.	1,4-Dioxane		2.72(1)	-1.06	-0.42[e]	-0.20	-0.07
27.	Dursban [j]		10.10(2)	0.85	5.04[k]	-0.27	-0.37
28.	Fenuron [l]		3.45(1)	-0.42	0.98[e]	0.47	0.26
29.	Hexachlorobenzene		43.0 (2)	1.52	6.22[m]	0.30	0.26
30.	Hexachlorocyclopentadiene		14.40(2)	1.02	5.04[n]	0.17	0.09
31.	Lindane (γ-BHC)		4.85(2)	0.46	3.72[o]	0.03	-0.10
32.	Nitrobenzene		4.00(1)	-0.22	1.85[e]	0.13	-0.07
33.	Phenazine		4.10(2)	0.36	2.84[e]	0.65	0.51
34.	1,2,4,5-Tetrachlorobenzene		23.3 (1)	0.91	4.67[m]	0.26	0.16
35.	Toluene		6.65(2)	0.22	2.69[e]	0.43	0.28
36.	1,2,4-Trichlorobenzene		14.00(1)	0.66	4.18[m]	0.09	-0.02
37.	Trichloroethylene		3.15(2)	0.18	2.42[h]	0.60	0.44
					Av (n=22)	0.27	(n=37) 0.19

[a]Flow rate in parentheses, mL/min. [b]Calculated log K_{ow} (using specified regression equation) minus Literature log K_{ow}. [c]Brown and Flagg (5). [d]Karickhoff et al. (4). [e]Leo et al. (1). [f]Value for naphthalene, +0.71 for Cl substituent (1). [g]Kenaga (20). [h]Banerjee et al. (21). [i]Banerjee (22). [j]O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl)phosphorothioate. [k]Macalady (23). [l]3-phenyl-1,1-dimethylurea. [m]Kenaga and Goring (9). [n]Wolfe et al. (24). [o]Kurihara et al. (25).

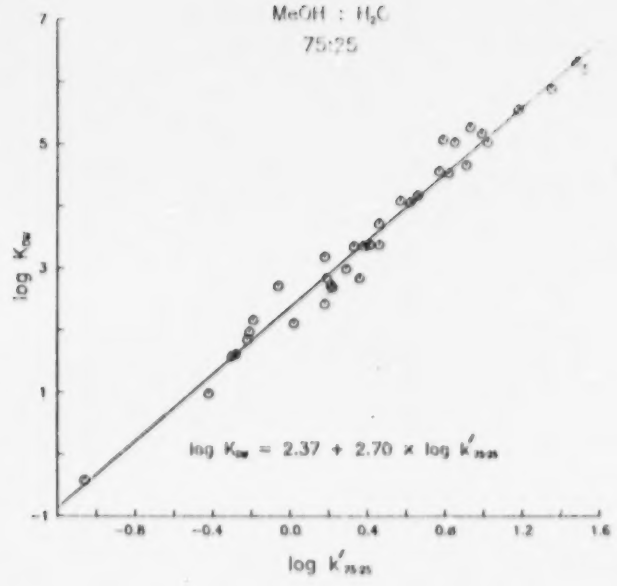

Figure 3. Correlation Plot for K_{OW} - k' Data on 37 Organic Solutes

with an average alog K_{OW} (Table I, Column 6) of 0.19 and a standard deviation for alog K_{OW} of 0.25. This is equivalent to an error factor of 1.8 in determining K_{OW}. (Neither the slope nor the intercept of eq. 4 is significantly different from that of eq. 6, at the 95 confidence level.)

Features of the HPLC Method

The correlation between log K_{OW} and log $k'_{75:25}$ is reasonably satisfactory for estimating the approximate K_{OW}'s of organic solutes for environmental modeling purposes. If further improvement were necessary, a stronger correlation might be obtained using a 70:30 or a 65:35 (v/v) solvent mixture, but as the %H_2O is increased (a) the t_R may become so long as to be impracticable, and (b) solutes of low solubility will be more likely to precipitate in the column. Other reverse-phase columns (e.g., C_8-) might also be tried.

In actual practice, a group of 6 to 8 standards would probably be used to establish a working calibration curve. Concerning the precision of measuring log K_{OW}'s by the HPLC technique, both t_R and t_C can be estimated within ±0.05 min., so for all but the shortest t_R values, log k' is determined to ±0.02. Thus, log K_{OW}'s are calculated to ±0.05 units, but with additional uncertainty, of course, from the constants used in the correlation equation. Solvent composition is relatively critical: a 2% change in the solvent mixture (from 75:25 to 73:27) decreased both the slope and the intercept of the log K_{OW}-log k' plot by about 5% for an aromatic hydrocarbon test group (benzene, naphthalene, phenanthrene, and pyrene), compared with the normal precision of ± 2% in measuring slope and intercept.

Column degradation over a period of 6 months caused a significant shift in the calibration line: shorter retention times were observed, leading to smaller log k' values, with a 5% increase in the slope of a log K_{OW}-log k' plot, and a 10% increase in the intercept. Changes over a period of days or weeks can be monitored using phenanthrene or a similar solute as internal reference, adjusting the log k' values based on the shift in that for phenanthrene. Periodically, however, the group of standards should be chromatographed to establish a new calibration line. A second C-18 column from the same manufacturer had a somewhat greater

capacity and gave t_0 values, correlation slope, and correlation intercept that were all about 8% lower than for the first column before it degraded.

This chromatographic method is restricted to neutral, relatively non-polar molecules. If a compound (e.g., monoprotic acid or base) ionizes appreciably in the eluting solvent, its true k' cannot be measured unless the solvent is buffered and the apparent k' corrected for the fraction ionized, α: $k'_{true} = k'_{app}/(1-\alpha)$, assuming the ionized product is not retained by the column. The compound 2,4-D [pK_a in H_2O of 2.64 (26); estimated pK_a in 75:25 MeOH-H_2O of ~4.0] gave an apparent k' of 0.28, but if the solute was ~ 75% ionized after injection of the 0.2 mM solution onto the column, one would calculate a true k' of 1.12, yielding an estimated log K_{OW} of 2.49, closer to the literature value of 2.81 (1).

Interpretation of the Correlation Slope

It is of interest to determine whether the slope of 2.70 in eq. 6 can be derived from solution theory. In reverse-phase chromatography, k' for a solute is directly proportional to its partition coefficient between the C-18 stationary phase, s, and the mobile phase, m. Hence k' is proportional to X_s/X_m, where X_s and X_m represent mole fraction solute concentrations in the respective phases as the solute moves through the chromatographic column. [Both X_s and X_m vary across a peak, but for relatively non-polar solutes that follow Henry's law (i.e., constant activity coefficients), the ratio X_s/X_m is independent of total solute concentration up to the point of saturation.] Substituting this relationship in eq. 3, and rearranging, gives the equation

$$(1/b_m) \log K_{OW} = \log (X_s/X_m) + c_m \qquad (7)$$

where b_m denotes the slope of the log K_{OW}-log k' correlation plot for a given mobile phase and c_m is the intercept divided by b_m. For 100% H_2O as mobile phase, denoted by the subscript w, we have the analogous equation

$$(1/b_w) \log K_{OW} = \log (X_s/X_w) + c_w \qquad (8)$$

Subtracting eq. 7 from eq. 8 and canceling the X_s terms (i.e., assuming that most of the solute is in the stationary phase, for each mobile phase), gives the equation

$$[(1/b_w) - (1/b_m)] \log K_{OW} = \log (X_m/X_w) + (c_w - c_m) \qquad (9)$$

which shows that the change in slopes of the log K_{OW}-log k' plots with change in mobile phase composition is related to the change in ratio of X-values (or, alternatively, the change in ratio of activity coefficients).

As indicated above, the ratio X_m/X_w for a solute is equal to the ratio of its solubilities in the respective phases. Data available for five solutes in 75:25 MeOH-H_2O and in 100% H_2O (27,28) were plotted in Figure 4 according to a rearranged eq. 9, with slope of $1/[(1/b_w)-(1/b_m)]$. The regression line had a slope (± std. dev.) of 1.41 ± 0.18, and correlation coefficient of 0.95. From this slope, assuming $b_w = 1.00$ for the log K_{OW}-log k' correlation with H_2O as mobile phase (14-16), one calculates a b_m value of 3.44, in rough agreement with the experimental value of 2.70.

The above comparison of chromatographic and octanol/water experiments assumes an equivalent state for the solute in the C-18 and in the octanol phases. Yalkowsky and Valvani (29) correlated K_{OW} and aqueous solubility data for over a hundred liquids; their equation, analogous to a plot of eq. 8, had a slope yielding the value 0.92 for b_w. Similarly, Banerjee et al. (21) reported a b_w value of 0.89 from a study of 27 compounds. The deviation of these slopes from unity has been attributed to increased solute-solute interactions in the octanol phase on going to compounds of higher solubilities (29). Using the average K_{OW}-solubility correlation value for b_w of 0.90, the above slope of 1.41 yields a b_m value of 2.50, in close agreement with our value of 2.70. This appears to validate the assumption that changes in ratios of X-values from solute to solute are the primary factors in controlling the changes in log k' values, the activity coefficients in the stationary phase (or in octanol) not changing much as the mobile phase changes from 75:25 MeOH-H_2O to 100% H_2O.

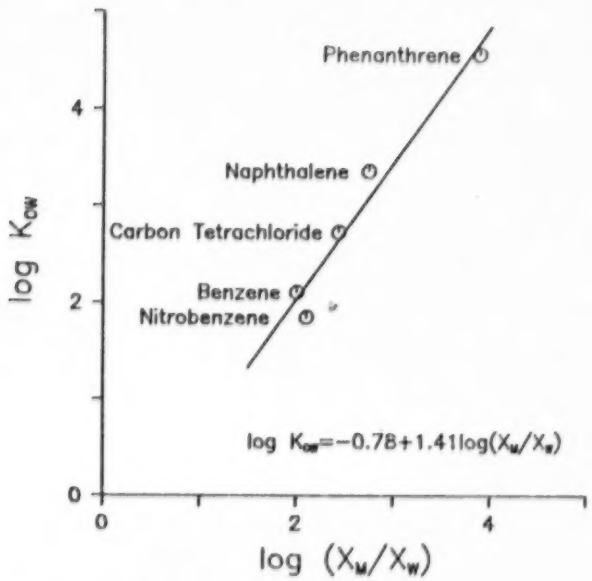

Figure 4. Relationship of K_{OW} to Solute Solubility Ratios
X_m/X_w = ratio of solubility in 75:25 MeOH-H_2O to that in water.

Estimation of Log Kow for Other Organic Solutes

Chromatographic data for 25 compounds whose K_{OW}'s have not been directly measured are presented in Table II. Included are 6 halogenated aliphatics, 12 halogenated aromatics and aromatic/aliphatic derivatives, 4 phthalate esters, and 3 cyclic aliphatic derivatives. Results for log K_{OW} by the HPLC method are compared where possible to other estimated values, primarily those calculated using the group additivity-constitutive methods of Hansch and others, as described by Yalkowsky and Morozowich (3).

In general the agreement between HPLC and calculated log K_{OW} values is within 1.00 log units. For polyhalogenated aliphatics (compounds numbered 14, 15, 21, 23, and 25 in Table II), agreement is better with the Hansch than with the Nys and Rekker calculated values, which are 2 to 4 log units lower than the HPLC values. It appears that the Nys and Rekker constants for aliphatic Cl and F are low for these polyhalogenated molecules. Even by the Hansch method, agreement with HPLC is poor for tetrachloroethylene and for 1,1,2-trichloro-trifluorethane.

The HPLC values are distinctly lower than the calculated values for the halogenated biphenyls (Nos. 3, 17, 18, 19, and 20), all of which had at least one ortho chlorine atom. For No. 18 and No. 19, derived experimental values of 5.2 agree roughly with the HPLC estimates; for No. 20, with four o-Cl atoms, the HPLC value is 3 log units lower than the calculated value. In these cases, the calculation methods do not differentiate between the position isomers (Nos. 18, 19, 20), whereas elution chromatography -- both liquid and gas (31) -- show large differences, which presumably will be reflected in different K_{OW} values. A trend toward low HPLC values is noted also for DDT-type compounds (Nos. 7, 8, 16). Finally, the HPLC value of 8.06 for di-n-octylphthalate is much higher than the solubility-derived value of 4.60; agreement with the HPLC value, as was found for the diethyl and dibutyl esters, would require a dioctylphthalate solubility lower by five or six orders of magnitude than that reported by Wolfe *et al.* (30).

Table II. Estimation of Log K_{ow} for Additional Organic Solutes

No.	Compound	75:25 Medium t_R[a] (min)	75:25 Medium log k'	Est. log K_{ow} (Eq. 6)	Other Estimates of log K_{ow} Calc.[b]	Calc.[c]	Exptl.
1.	1-Bromodecane	41.0 (2)	1.59	6.43	5.66	5.68	
2.	Butylbenzylphthalate	12.25(1)	0.59	3.97	4.44[d]	4.08[d]	
3.	2-Chlorobiphenyl	6.75(2)	0.64	4.10	4.85[e]	4.82[e]	
4.	Cyclododecane epoxide	9.30(2)	0.86	4.70	--	--	
5.	Cyclododecanone	6.15(2)	0.64	4.10	4.20	4.14	
6.	1,5,9-cyclododecatriene	19.20(2)[f]	1.21	5.65	5.10	5.34	
7.	p,p'-DDD	10.60(2)	0.87	4.73	5.18[g]	5.71[g]	
8.	p,p'-DDE	26.0 (2)	1.30	5.89	4.88[g]	5.01[g]	
9.	2,4-D Octyl ester	25.6 (2)	1.29	5.86	6.71[h]	6.89[h]	
10.	Di-n-butylphthalate	6.80(2)	0.65	4.13	4.29[d]	4.47[d]	4.12[i]
11.	Diethylphthalate	4.70(1)	-0.06	2.21	2.29[d]	2.35[d]	2.97[i]
12.	Di-n-octylphthalate	158.0 (2)	2.10	8.06	8.29[d]	8.71[d]	4.60[i]
13.	2,5-Di-(p-fluorophenyl)-furan	28.0 (1)	1.01	5.11	5.6[j]	5.0[j]	
14.	Heptachlor	16.05(2)	1.07	5.27	6.06	2.19	
15.	Hexachloroethane	12.80(1)	0.61	4.04	3.34	0.56	
16.	Methoxychlor-DDD	5.35(2)	0.52	3.78	4.69[k]	5.22[k]	
17.	2,2'-PCB	6.25(2)	0.60	4.00	5.61[e]	5.55[e]	
18.	2,4,2',4'-PCB	22.0 (2)	1.22	5.68	7.13[e]	7.01[e]	5.2[l]
19.	2,5,3',4'-PCB	27.6 (2)	1.32	5.95	7.13[e]	7.01[e]	5.2[l]
20.	2,6,2',6'-PCB	6.95(2)	0.66	4.16	7.13[e]	7.01[e]	
21.	Pentachloroethane	3.50(2)	0.25	3.05	2.95	0.70	
22.	Pentachloronitrobenzene	15.30(2)	1.05	5.21	5.43[m]	5.31[m]	5.01[m,n]
23.	Tetrachloroethylene	5.40(2)	0.52	3.78	2.26	0.57	2.53[o]
24.	1,2,3-Trichlorobenzene	12.70(1)	0.61	4.02	4.39[p]	4.30[p]	
25.	1,1,2-Trichloro-trifluoroethane	7.35(1)	0.29	3.16	1.66	-0.85	

[a]Flow rates in parentheses, mL/min. [b]Method of Hansch et al., as summarized by Yalkowsky and Morozowich (3). [c]Method of Nys and Rekker, as summarized by Yalkowsky and Morozowich (3). [d]Using o-phthalic acid (log K_{ow} 0.29) as parent molecule (1). [e]Using biphenyl (log K_{ow} 4.09) as parent molecule (1). [f]Av. for two major isomers with equal detector responses. [g]Using p,p'-DDT (log K_{ow} 5 57) as parent molecule (20). [h]Using 2,4-D (log K_{ow} = 2.81) as parent molecule, with change from -COOH to $-COOC_8H_{17}$ based on $CH_3COOH \longrightarrow CH_3COOC_2H_5$ data, plus 6 CH_2's (1). [i]Using aqueous solubilities (30), and K_{ow}-solubility correlation equations of Karickhoff et al. (4). [j]Using 1.04 for log K_{ow} of furan, the parent molecule. [k]Using methoxychlor (log K_{ow} 5.08) as parent molecule (4). [l]Using partition coefficients to sediments (19), % organic carbon, and correlation equations of Karickhoff et al. (4). [m]Using p-chloronitrobenzene (log K_{ow} 2.39) as parent compound (1). [n]Adding difference between pentachlorophenol and p-chlorophenol as 4 Cl's (1). [o]Direct measurement (21). [p]Using benzene (log K_{ow} 2.11) as parent molecule (4).

Some small polar molecules (e.g., acetonitrile, acrylonitrile, acetone, 2-butanone) give HPLC results that are higher than directly measured K_{ow}'s by about 1 or 2 log units. This may reflect the relative tendencies of these solutes to solvate in the various phases, lowering the activity coefficients, and could even be an indication of speciation. For hydrophobic organics, however, the HPLC method offers a convenient experimental route to the accurate estimation of K_{ow} values.

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